The Growth Model of CdTe Thin Film by Close Spaced Sublimation

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***Abstract*—Close spaced sublimation (CSS) has attractive features for high-rate deposition of CdS/CdTe thin film solar modules. CSS has been successfully implemented in commercial production of CdTe solar panels with size of 0.6 m x 1.2 m and 1.2 m x 1.6 m. A CSS growth model is a useful tool to guide the CdTe thin film deposition and the design of CSS. In this paper, a growth model was developed for CdTe deposition including diffusion limited, sublimation limited and reaction limited with the presence of oxygen. The model can explain the effect of source and substrate temperature, ambient gas pressure and the separation between source and substrate on the growth rate of CdTe by CSS. The model may prove very useful for optimization of the CSS process with respect to its design variables (pressure, temperature, etc.).**

***Index Terms* — CSS, CdS/CdTe, growth model**

I. Introduction

Cadmium telluride (CdTe) thin film photovoltaic has been shown to be the most promising solar cells because of its long term stable performance [1], easy scale-up for large area production, high absorption coefficient and optimum band gap. Due to the high absorption coefficient and optimum band gap of CdTe, a film thickness of 2 μm should be sufficient to absorb most of the solar spectrum. Compare to several hundred micrometer silicon solar cell, it reduced many materials and save lots of cost. In 2015, a new world record conversion efficiency 21.5% for CdTe solar was announced by First Solar. Besides, a new world record for cadmium-telluride (CdTe) photovoltaic (PV) module conversion efficiency 17.5% was reached. CdTe thin films solar cell has been deposited by several techniques, such as electrodeposition [2], chemical bath deposition [3], physical vapor deposition [4], RF and DC sputtering [5], pulsed LASER deposition [6], OMVPE [7], screen printing [8], close-space-sublimation (CSS) [9] and Vapor Transport Deposition (VTD). Among the methods, CSS and VTD technique are expected to have the highest deposition rate and were successfully used in industry. Compare to the successful VTD by First Solar, the CSS by Abound, GE and CTF didn't success as we expected. There are many reasons about the failure of CSS in industry. One of the reasons is because the growth model of CSS is still confused. This paper proposes a growth model to explain the growth of CdTe which was confirmed by the experimental work of Dr. Rose in his Ph.D thesis.

II. Experimental

We cut glass to 4*6 inch. The glass is cleaned by sonication in a 1% solution of Liquinox soap in hot DI water. The CdS was deposited on the cleaned substrates by CBD [10]. The CdS substrate is then loaded in the deposition chamber as shown in. Fig.1 and Fig. 2.

Fig. 1. CSS deposition system

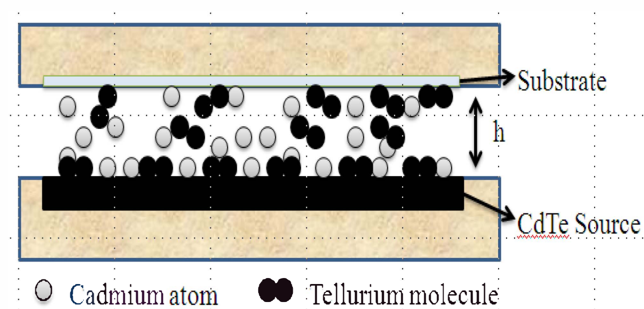

Fig. 2. Schematic diagram of CSS deposition chamber

The CdS substrate was annealed at 400 °C for 15 min in 30 torr H2 to reduce oxygen-related defects. After cooling to 200°C, the CdTe deposition sequence is initiated. The CdTe deposition by CSS is based on the principle of reversible dissociation of CdTe at high temperatures. Then the elemental gases diffuse to the substrate and the gases recombine on the substrate with lower temperature than the source. The CdTe deposition chemical process equation by CSS is below:

A. $$CdTe(s) \rightarrow Cd(g) + \frac{1}{2}Te_2(g)$$

In the source, CdTe decomposes at the source temperature .

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The equilibrium constant is:

$$K_{CdTe}(T_{Sou}) = P_{Cd}(0)P_{Te_2}(0)^{1/2}$$

where $P_{cd}(0)$ and $P_{Te2}(0)$ are the equilibrium pressure of Cd and Te_2 at the temperature of source T_{sou}. The equilibrium constant can be calculated from the expression given by deLargy et al.

$$K_{CdTe}(T_{Sou}) = P_{Cd}(0)P_{Te_2}(0)^{1/2} = \exp[\frac{-\Delta G_{CdTe(T_{Sou})}}{RT_{Sou}}] \quad (1)$$

$$\Delta G_{CdTe(T_{Sub})} = 68.64 - 44.94\times10^{-3}\mathrm{T\ kcal/mol}$$

B. $$Cd(g) + \frac{1}{2}Te_2(g) \rightarrow CdTe(s)$$

In the substrate, the Cd and Te_2 combines into CdTe at substrate temperature T_{sub}. The equilibrium constant is:

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2}$$

where $P_{cd}(h)$ and $P_{Te2}(h)$ are the equilibrium pressure of Cd and Te_2 at the temperature of substrate T_{sub}. The equilibrium constant is:

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2} = \exp[\frac{-\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}] \quad (2)$$

III, GROWTH MODEL

The growth model of CdTe is very complicated. To simplify the growth model, we just consider the situation of steady state, stochiometrical CdTe deposition. The growth rate depends on several interrelated parameters: the space between the source and the substrate, the temperatures of the source Tso and the substrate Tsub, and the pressure, temperature and composition of gases in the deposition chamber. According to different situation, we classify the growth model into three parts:

A. Sublimation model

If the mean free path of Cd atoms and Te2 molecules is longer than the space between the source and substrate (λ >h), then it is sublimation model.

$$\lambda = \frac{KT}{\sqrt{2}\pi d^2 P} \quad (3)$$

where k is Boltzmann's constant, P is the pressure (Pa), T is the source temperature (K) and d is the molecular diameter of Cd and Te_2.

In the sublimation model, the growth rate is proportional to the equilibrium vapor pressure difference between the source and the substrate.

$$G_{Subi}(m/s) = \frac{\alpha\beta(P^i_{sou}T_{sou} - P^i_{sub}T_{sub})N_A}{\sqrt{\pi m_i RT_{av}}}(\frac{m_i}{\rho_i}) \quad (4)$$

where α and β are coefficients with values between 0 and1; P^i_{sou} and P^i_{sub} are the vapor pressure (Pa) of i in the source and substrate; mi represents the molar mass of the source material(kg/mol); R is the universal gas constant(J/(kgmol)); T_{sou}, T_{sub}, and T_{av} are the source, substrate, and average temperatures, respectively(K); NA is Avogadro's number; and ρ_i represents the density of the substance evaporated(kg/m3).

B. Diffusion model

If the mean free path of Cd atoms and Te_2 molecules is longer than the space between the source and substrate (λ <h), then it is diffusion model.

In the diffusion model, the growth rate can be calculated by Fick's law.

$$J_{cd} = \frac{D_{cd,j}}{khT_{ave}}(P_{Cd}(0) - P_{Cd}(h)) \quad (5)$$

Where k is Boltzmann's constant(J/K), T_{ave} is the average temperature between source and substrate, $D_{cd,j}$ is the binary coefficient of diffusion of cadmium diffusing into inert gas j (m2/s); This coefficient will be calculated using the Stefan–Boltzmann model given as

$$D_{Cd,j} = \frac{(NA(KT_{av}/\pi)^3 * (1/m_{Cd} + 1/m_j))^{1/2}}{3(P_{Cd,av} + P_j)\sigma^2_{Cd,j}} \quad (6)$$

where m_{Cd} and m_j are the molar masses of cadmium and helium (kg/mol), $P_{Cd,av}$ is the vapor pressure(Pa) of Cd evaluated at the average of the substrate and source temperatures T_{av} (K), P_i is the chamber pressure(Pa), NA is Avogadro's number, K is Boltzmann constant, and $\sigma_{Cd,j}$ is the average molecular diameter.

$$\sigma_{Cd,j} = \frac{\sigma_{Cd} + \sigma_j}{2}$$

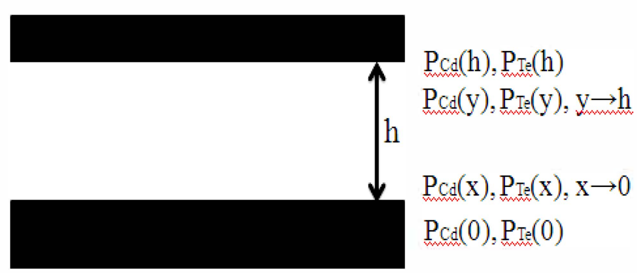

Fig. 3. The diagram of CSS deposition model

η is the deposition efficiency. It is an empirical constant that adjust the model's output to match experimental data.

So the diffusion model can be summarized as 10 equations with 10 unknown: $P_{Cd}(0)$ $P_{Te_2}(0)$ $P_{Cd}(x)$ $P_{Cd}(y)$ $P_{Te_2}(x)$ $P_{Te_2}(y)$ $P_{Cd}(h)$ $P_{Te_2}(h)$ J_{cd} J_{Te_2}

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$$K_{CdTe}(T_{Sou}) = P_{Cd}(0)P_{Te_2}(0)^{1/2} = \exp[\frac{-\Delta G_{CdTe(T_{Sou})}}{RT_{Sou}}] \quad (1)$$

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2} = \exp[\frac{-\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}] \quad (2)$$

$$P_{Cd}(0) = 2P_{Te_2}(0) \quad (3)$$

$$P_{Cd}(h) = 2P_{Te_2}(h) \quad (4)$$

$$\lim_{x\to 0} P_{Cd}(x) = P_{Cd}(0) \quad (5)$$

$$\lim_{x\to 0} P_{Te_2}(x) = P_{Te_2}(0) \quad (6)$$

$$\lim_{y\to h} P_{Cd}(y) = P_{Cd}(h) \quad (7)$$

$$\lim_{y\to h} P_{Te_2}(y) = P_{Te_2}(h) \quad (8)$$

$$J_{cd} = \frac{D_{cd,j}}{khT_{ave}}(P_{Cd}(\mathrm{x}) - P_{Cd}(\mathrm{y})) \quad (9)$$

$$J_{Te_2} = \frac{D_{Te_2,j}}{khT_{ave}}(P_{Te_2}(x) - P_{Te_2}(y)) \quad (10)$$

Since Cd atom diffuse much faster than Te_2 molecular, the final deposition rate is determined by the diffusion of Te2 molecular. According to the Rose's paper, if the

T_{sub}=600°C; T_{sou}=640°C; h=2mm, the deposition rate is about 4.33um/min. If we put their data into our equation, we can calculate the deposition rate is about 17.03um/min. The efficient η =4.33/17.031= 25.4%.

Figure 4 shows that the growth rate almost kept the same with the increase of T_{sub} when the T_{sub} is below to 550°C. The growth rate decrease greatly with the increase of T_{sub} when the T_{sub} is above to 550°C. It is because of the resublimation of CdTe on the substrate.

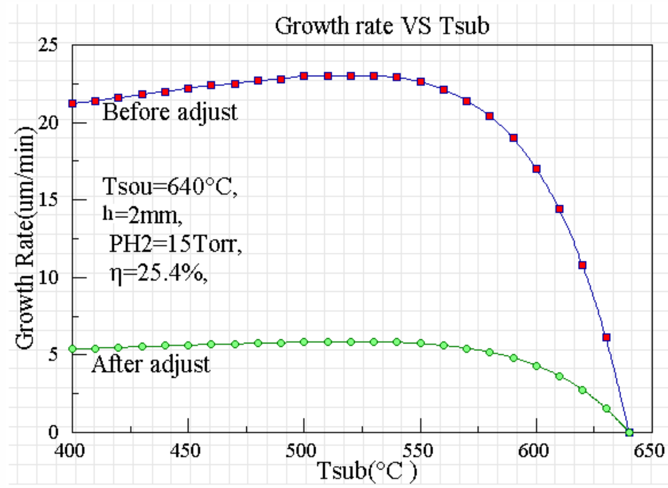

Fig. 4. The growth rate at different substrate temperature

Figure 5 shows that the adjusted growth rate is very close to the experimental data. It means that the diffusion model is very accurate.

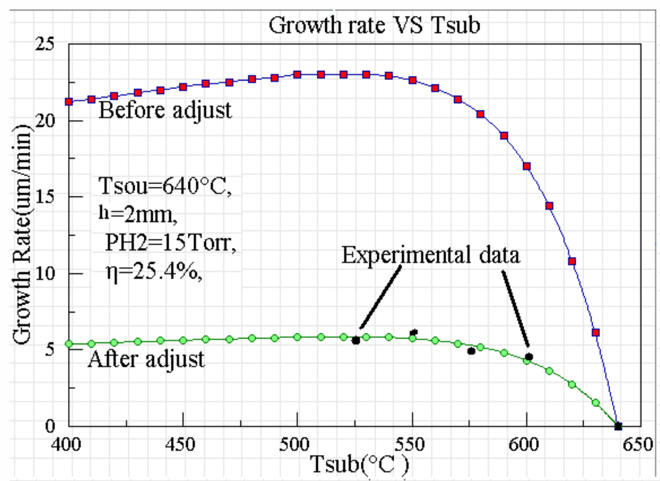

TABLE I

THE IDEA DEPOSITION RATE AND ADJUSTED DEPOSITION RATE AT DIFFERENT TEMPERATURE

T_{sub} (°C)	400	410	420	430	440	450	460	470	480	490	500	510	520
R_{Ideal}(um/min)	21.2	21.4	21.6	21.8	22	22.2	22.4	22.5	22.7	22.8	23	23	23
$R_{Adj.}$ (um/min)	5.38	5.43	5.48	5.54	5.59	5.64	5.68	5.73	5.76	5.8	5.83	5.85	5.86

T_{sub} (°C)	530	540	550	560	570	580	590	600	610	620	630	640
R_{Ideal}(um/min)	23	22.9	22.6	22.1	21.4	20.4	19	17	14.4	10.8	6.13	0
$R_{Adj.}$ (um/min)	5.85	5.81	5.74	5.63	5.44	5.19	4.83	4.32	3.65	2.75	1.55	0

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C. Reaction model

Since oxygen plays an important role for high efficiency CdTe and it used to be input with inert gas into the crucible, it is necessary to consider the effect of oxygen to the growth rate.

$$CdTe(s) \rightarrow Cd(g) + \frac{1}{2}Te_2(g)$$

$$Cd(g) + \frac{1}{2}Te_2(g) \rightarrow CdTe(s)$$

$$Cd(g) + \frac{1}{2}O_2(g) \rightarrow CdO(s)$$

$$Te_2(g) + 2O_2(g) \rightarrow 2TeO_2(s)$$

Since the TeO_2 is much less than CdO, we neglect the effect of TeO_2 and only focus on the reaction of Cd and O_2. Besides, the CdO in the source is much more than CdO in the substrate, we will also neglect the effect of CdO in the substrate. The equation was simplified to the following:

$$K_{CdTe}(T_{Sou}) = P_{Cd}(0)P_{Te_2}(0)^{1/2} = \exp[\frac{-\Delta G_{CdTe(T_{Sou})}}{RT_{Sou}}] \quad (1)$$

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2} = \exp[\frac{-\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}] \quad (2)$$

$$P_{Cd}(0) = 2P_{Te_2}(0) \quad (3)$$

$$P_{Cd}(h) = 2P_{Te_2}(h) \quad (4)$$

$$\lim_{x\rightarrow 0} P_{Cd}(x) = P_{Cd}(0) \quad (5)$$

$$\lim_{x\rightarrow 0} P_{Te_2}(x) = P_{Te_2}(0) \quad (6)$$

$$\lim_{y\rightarrow h} P_{Cd}(y) = P_{Cd}(h) \quad (7)$$

$$\lim_{y\rightarrow h} P_{Te_2}(y) = P_{Te_2}(h) \quad (8)$$

$$J_{cd} = \frac{D_{cd,j}}{khT_{ave}}(P_{Cd}(\mathrm{x}) - P_{Cd_{O2}}(0) - P_{Cd}(\mathrm{y})) \quad (9)$$

$$J_{Te_2} = \frac{D_{Te_2,j}}{khT_{ave}}(P_{Te_2}(x) - P_{Te_2}(y)) \quad (10)$$

$$K_{CdO} = P_{Cd}(0)P_{O_2}(0)^{1/2} = \exp[\frac{-\Delta G_{CdO(T_{Sou})}}{RT_{Sou}}] \quad (11)$$

$$\log_{10}^{K_{CdO}(T_{Sou})} = \left\{-\frac{1.98*10^4}{T} + 11.7\right\} \quad (12)$$

T_{Sou} =640°C, T_{Sub} = 525°C, h=2mm, P_{H2}=15Torr, η=25.4%

TABLE II
THE GROWTH RATE IN REACTION MODEL

P_{O2}(Torr)	0	0.2	0.5	1
R_{Ideal}(um/min)	23	21.4	19.2	16.2
R_{Adjust} (um/min)	5.84	5.43	4.87	4.11
$R_{exp.}$ (um/min)	5.72	5.45.	4.67	4.2

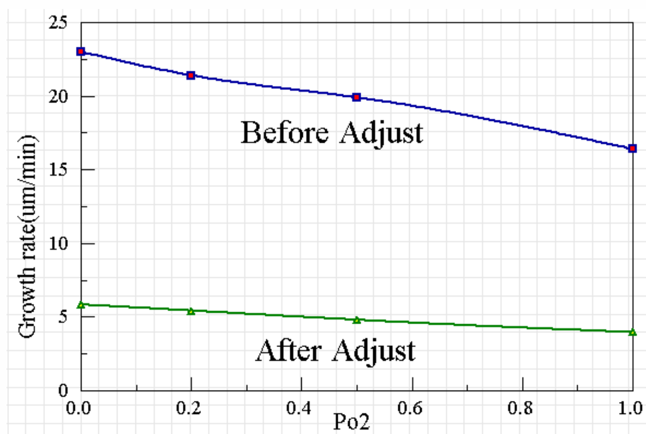

Fig. 6 The growth rate at different P_{O2}

Figure 6 shows that the growth rate decrease with the increase of P_{O2}, because the increase of P_{O2} react with more Cd and Te_2. So the growth rate decreased.

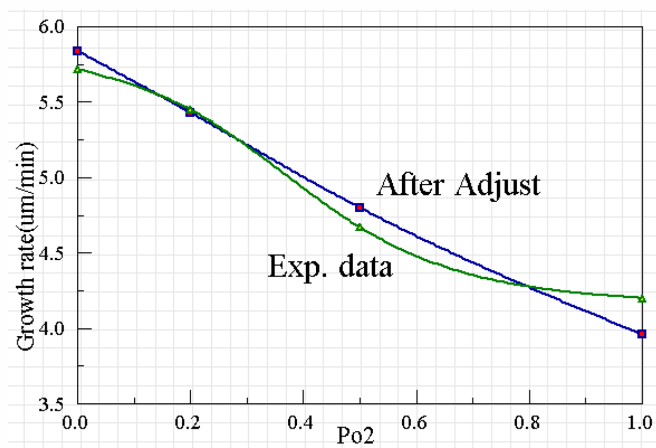

Fig. 7 The compare of adjusted growth rate and the experimental data

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Figure 7 shows that the adjusted data is very close to the experimental data. So the reaction growth model is very accurate.

VI. CONCLUSION

In this paper, we present three different growth models in CdTe deposition by CSS. We present mean free path to decide the sublimation and diffusion model. If the mean free path of Cd atoms and Te2 molecules is shorter than the space between the source and substrate (λ <h), it is sublimation model. If λ >h, it is diffusion model. If the inert gas has oxygen input, then we need to consider the reaction model. The growth models are affected by several important parameters: spacing, ambient gas, ambient gas pressure, substrate temperature and source temperature. They all have independent control over the growth rate.

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